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THE RATE OF SEDIMENTATION OF KAOLIN SUSPENSIONS AS AFFECTED BY SALTS AT VARYING HYDROGEN ION CONCENTRATIONS.

T H E S I S

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by

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C O N T E N T S.

THE RATE OF SEDIMENTATION OF KAOLIN SUSPENSIONS AS AFFECTED BY SALTS AT VARYING HYDROGEN ION CONCENTRATIONS,

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A study of the rate of sedimentation of suspensions is of interest from the point of view of the general theories of the stability of particles in suspension and also from the point of view of many problems of practical importance such as the flocculation of heavy soils, the mechanical analysis of soils, and the clearing of drinking waters. It is well known that electrolytes affect the rate of sedimentation of suspensions, and a great deal of work has been described in which the concentration of the electrolyte present has been varied and the resulting rates of sedimentation compared, but experiments in which two factors have been varied simultaneously do not appear to be so numerous.

In 1848 Fr. Schulze observed that the rate of sedimentation of turbid particles is greater in solutions of calcium hydroxide and ammonium carbonate than it is in pure water or in solutions of ammonium hydroxide. A similar observation was made by Sheerer (1850). Schulze (1866) later recorded the results /

results of some experiments on the quantities of calcium and magnesium salts necessary for the flocculation of clay suspensions, but drew no general conclusions from his results. Schloesing (1870) working on suspensions of soil clay showed that small quantities of salts were capable of bringing about complete flocculation and that the quantities varied for different salts. Mayer (1879) also working on suspensions of soil clay noted that the rate of sedimentation of clay particles in solutions of alkalies and of salts giving an alkaline reaction is no greater than it is in pure water, whereas with mineral acids and their salts it is markedly increased. The increase in the rate of sedimentation of suspensions produced by acids and neutral salts and the counteraction of flocculation produced by alkali hydroxides and carbonates was emphasised by Hilgard (1879), who worked on methods of mechanical analysis of soils.

The difference between electrolytes and non-electrolytes was clearly brought out in the experiments of Bodländer (1893) who showed that electrolytes could sediment kaolin suspensions while non-electrolytes could not. Bodländer also demonstrated the fact that there is for each electrolyte a certain concentration below which flocculation is not produced. He compared the flocculating effects of various electrolytes, and his results /

results show that acids and salts of bi- and tervalent metals are good flocculators of kaolin suspensions, while relatively very large quantities of alkalies are required to bring about the same degree of sedimentation. His experimental data are in approximate agreement with Schulze's Law (1882 and 1884), elaborated by Picton and Linder (1895), Hardy (1899 and 1900), and mathematically deduced by Whetham (1899), that the precipitating power of an ion for suspensions is a function of its valency. Hardy by careful quantitative measurements showed that the active ion is that one whose electrical charge is of opposite sign to that of the particles precipitated. Spring (1900) observed that the sedimenting power of a salt for clay suspensions depended on the cation and its valency. Hall and Morison (1907-8) in an investigation of the flocculation of kaolin suspensions found the flocculating effect of tervalent cations was greater than that of bivalent, while these in turn were more effective than univalent ions, but they found no evidence for the ratios demanded by the "Valency Law". The best flocculators were the free acids, Hydrochloric acid, Nitric acid, and Sulphuric acid, which were always more effective than their salts. The flocculating power of a cation was not independent of the anion present with it. The relative effectiveness of the three acids was Hydrochloric acid 20, Nitric acid 19, Sulphuric /

Sulphuric acid 13. The same relation was obtained whether the free acids or their salts were used. The univalent cations were not equally effective, potassium being about twice as effective as sodium, and the effect of the hydrogen ion ten times greater still. Other acids - acetic, oxalic, tartaric, and citric - showed flocculating powers in the ratios 9 : 2·5 : 2·5 : 0. Wolkoff (1916) also found no correspondence with the requirements of the Valency Law when he treated suspensions of kaolin, of subsoil clay and of various soils with a large number of different electrolytes. His results further show that the efficiency of the same electrolyte with different suspensions varies considerably, depending largely upon the chemical composition of the suspended material. This has not always been recognised, and too great readiness has frequently been shown to draw general conclusions for all clay suspensions from the results of experiments on suspensions of one particular clay. Recent researches such as those of Hall and Russell (1911), Hendrick and Ogg (1916), Robinson (1917), Blanck (1918), and Joseph and Hancock (1924) show that the chemical composition of different clays varies very greatly. When attempts are made to correlate the results of different workers on the sedimentation of clay suspensions, a further complication arises in the fact that the term "clay" is used in many senses. In this country /

country in soil investigations the mineral fraction of the soil consisting of particles less than 0·002 mm. in diameter is designated clay, while in the United States of America the upper limit of particle size for the same fraction is 0·005 mm.: in ceramic work material consisting of particles less than 0·1 mm. in diameter would be classed as "clay", while at the other extreme it is possible to obtain true colloidal suspensions of clay containing only ultramicroscopic particles. It seems necessary to use the term "clay" for all fine-grained material of an alumino-silicate nature, and to distinguish between different types of clay with regard to chemical composition and particle size. Joseph and Hancock (loc. cit.) emphasise the importance of the silica-alumina ratio, which seems connected with essential "clay" properties, being, for instance, low in non-plastic and high in plastic materials.

The interpretation of experiments on the effect of salts on the rate of sedimentation of clay suspensions is never simple owing to the fact that an exchange of bases may take place between the clay particles and the salt solution added, so that part of the flocculation which results may be due to ions brought into solution by the base exchange. Attention was drawn to this by Comber (1921) and has since received confirmation /

confirmation in the recent researches of Gedroiz (1921-23) and of Wiegner (1925). Gedroiz (1915) in the course of an extensive series of experiments on the action of electrolytes on soil clay suspensions, pointed out the importance of base exchange, but owing to the fact that the results were published as a Communication of the Petrograd Bureau of Agriculture and written in the Russian language, his work did not become known in this country until within the last year or two.

In most of the former work on the subject of sedimentation the effect of the reaction of the system has either not been taken into account, or, where considered, has been expressed as normality of acid or alkali and not in terms of hydrogen ion concentration or pH. Bradfield (1923) has shown that while widely varying quantities of different acids were required to flocculate a soil clay suspension, the hydrogen ion concentration attained in each case was identical. He further showed that the hydrogen ion concentration had a great effect on the electrolyte requirement for flocculation. It appeared to be of interest, therefore, to carry out an extensive series of experiments on the rate of sedimentation of a suitable suspension where both the concentration of the salt present and the pH of the medium were simultaneously varied. For initial /

initial work it is advantageous to use a suspension of a comparatively simple nature and of known chemical composition. Kaolin was consequently chosen as approximately fulfilling these two conditions, although it is clearly recognised that it is by no means an inert substance (see for instance Sullivan (1907)). The limits of particle size were arbitrarily chosen so as to give a suitable type of suspension for the large number of experiments necessary.

EXPERIMENTAL.

The kaolin used was the ordinary commercially pure variety. Ten grams of this were triturated with a rubber pestle in a beaker containing 0·03 N ammonium hydroxide solution. The beaker was then filled to a depth of 8·5 cm. with the ammonium hydroxide solution and allowed to stand for 24 hours, when the supernatant liquid was decanted off. This process was repeated usually on five successive days, thus removing particles below 0·002 mm. diameter. It may be noted that the suspension obtained with the first washing is less dense than the succeeding ones, presumably because of the neutralisation of part of the ammonium hydroxide by acids in the kaolin. This neutralisation was shown by titration. The solid remaining in the beaker after these washings was then vigorously stirred up with 0·03 N ammonium hydroxide solution, the beaker was filled up to the 8·5 cm. mark with the same solution, and the suspension was allowed to sediment for 30 minutes. The supernatant suspension decanted off at the end of this period was used for the experiments described in this paper. Suspensions prepared in this way contained from 0·35 gm. to 0·52 gm. kaolin in 100 c.c. and were shown by titration to contain 0·025 N ammonium hydroxide, the pH being between 9 and 10. One cubic centimetre of suspension /

suspension diluted with its own volume of distilled water had cleared completely only after about 12 hours. After the addition of the various salt solutions used, readings were taken at the end of periods ranging from 5 to 15 minutes. At the end of such times no sediment had appeared in the control tube containing kaolin suspension and water.

Solutions of acid of various concentrations were prepared and 0·5 c.c. of these were added to each of a row of tubes. To each tube in the various rows was then added 0.5 c.c. of solutions of increasing concentration of the salt investigated. One cubic centimetre of the suspension was then rapidly added to each tube, and the tubes were shaken as nearly as possible all at the same time, allowed to stand, and readings of the degree of sedimentation taken. The shaking was repeated and a second reading taken after the tubes had stood for twelve or more hours. The second readings did not differ significantly from the first except in the cases of calcium sulphate and lanthanum chloride. These exceptions will be remarked upon later. The pH of the supernatant liquid was then determined colorimetrically.

The results are best represented in the series of figs. 1 - 22. All concentrations given are those of the 1 c.c. of solution to which 1 c.c. of kaolin suspension /

suspension was added. The whole area of each figure is divided by heavy lines into a number of regions. Each region corresponds to a particular degree of sedimentation, which is denoted by a Roman numeral according to the following convention:- The amount of precipitation after 15 minutes in the tube containing 0·06 N hydrochloric acid and no salt is denoted by IV. It was found that the opacity of the supernatant liquid in this tube corresponded to that of No.6 of a series of opacity tubes prepared as described by Brown (1919).* The reading of the tube to which neither acid nor salt has been added is denoted by 0, and intermediate degrees of sedimentation are indicated accordingly. Comparisons between the results of different experiments could be made by means of opacity tube readings. In cases where a combination of pH and salt gave a degree of sedimentation greater than that denoted by IV, numbers higher than four were employed to denote such degrees of sedimentation, for instance, where the opacity reading of the supernatant fluid was 2, as determined by Brown's tubes the sedimentation is denoted by VIII, and an opacity reading of 3 is denoted by VII. The pH values are shown in the

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* These tubes are prepared from a 1 per cent suspension of barium sulphate in a 1 per cent sodium citrate solution. This 1 per cent suspension is diluted with seven times its volume of 1 per cent sodium citrate solution. The tubes 1,2,3 .. 10 contain respectively 1 c.c.,2 c.c., 3 c.c. .. 10 c.c. of this 1 in 800 suspension made up to 10 c.c. with 1 per cent sodium citrate.

the figures by the ordinary numerals within brackets. Where a + or − sign occurs in the figures it refers to the nature of the electric charge on the particles as determined by cataphoresis.

DISCUSSION.

For purposes of discussion the salts investigated may be conveniently classified as containing uni-, bi-, or tervalent cations. These groups will, therefore, be considered separately.

Univalent Cations.

From consideration of figs. 1-10 it appears that the action of salts with univalent cations varies according as to whether the medium is alkaline or acid. At pH 2, for example, sodium chloride does not, in any concentration, increase the rate of sedimentation, and, in fact, in concentrations exceeding 0·085 N, causes considerable decrease. On the other hand, at pH 9 to 10 the same salt always causes an increase in the rate of sedimentation when present in concentrations greater than 0·085 N. Lower concentrations have little effect. The result of this is that although, where there is no salt, there is a very marked difference in the rate of sedimentation at a pH of 2 compared with that at a pH of 10, yet in presence of 0·171-0·342 N sodium chloride the rate of sedimentation is practically independent of the pH. If the sodium ion is coupled with a bivalent anion instead of a univalent one, that is, if sodium sulphate be used instead of sodium chloride, the same tendencies /

tendencies may be observed even though in a very much less marked degree.

This retardation of the rate of sedimentation in acid medium occurs also with lithium and ammonium chlorides at concentrations exceeding 0·063 N, although it is not so marked in these cases as with sodium chloride.

In alkaline medium, on the other hand, lithium chloride produces an increased rate of sedimentation when present in concentrations greater than 0·031 N, and the same effect is observed with ammonium chloride at pH 6 to 9. Lower concentrations of these salts have apparently no effect when the pH is above 7. In presence of 0·125 - 0·50 N solutions of the same salts the rate of sedimentation is practically independent of the pH. In all cases where a retardation of the rate of sedimentation occurred in acid medium the phenomenon was most marked at the beginning of sedimentation, while after half-an-hour the degree of precipitation tended to become the same at all concentrations of the salts. Potassium chloride at pH 9 to 10 and caesium chloride at pH 8 to 9 both cause a more marked increase in the rate of sedimentation than do the chlorides of the other univalent metals at the same equivalent concentration. This is evident on comparing the precipitation occurring when potassium chloride of 0·342 N is used with that occurring when sodium /

sodium chloride of the same normality is used. On the other hand neither potassium chloride nor caesium chloride has apparently any action in decreasing the rate of sedimentation at pH 2 to 3. From this it is evident that the effect of the chlorides of sodium, lithium and ammonium is one due to the cation and not to the anion. It is further clear that it is not due simply to the increase in density of the solution. The sedimenting actions of the univalent cations at half-normal concentration have been more closely determined and the results are given in fig. 6. It will be seen that the caesium ion has a slightly greater effect than the potassium ion in both acid and alkaline solution, while potassium in its turn is decidedly more effective than sodium.

The varied action of the univalent cations and the retardation of the rate of sedimentation observed with ammonium, sodium, and lithium chlorides in the presence of hydrochloric acid is presumably related to chemical actions taking place at the surface of the kaolin particles. It has already been pointed out that when an electrolyte is added to a suspension of kaolin an exchange of bases may take place between the added salt and the kaolin particles, and the resulting phenomena observed may be only partly brought about by the added cations. The cation which is absorbed by the particles may materially affect their properties /

properties, and the cations which are brought into solution, by means of the base exchange, may have a greater or less sedimenting action than those in the added salt solution. Gedroiz (1921-23 and 1924) has shown that great variations may occur in the physical properties of soil clay, according to the cation with which it is saturated. Clay saturated with sodium is more easily dispersed and is, in general, hydrophilic in character, whereas clay saturated with calcium is relatively hydrophobic and forms a less stable suspension. For the univalent ions the increase of dispersion is greatest with sodium and least with hydrogen, ammonium and potassium being intermediate in effect. This correlation between the univalent ions is exactly the same as that found for the action of electrolytes on clay suspensions. Wiegner (loc. cit.) points out that a satisfactory explanation of these phenomena can be found in the variations in the degree of hydration of the cations. He considers the clay particle to consist of a complex silicate nucleus carrying a negative charge and surrounded by a swarm of cations in dynamic equilibrium. The greater the valency and the less the hydration of these cations the greater will be the attractive force on them. When the outer layer consists of highly hydrated ions, the effective distance between the outer layer and the nucleus will be increased, and, in consequence /

consequence, the potential difference between the two layers will be increased. This increased potential will give rise to a greater stability in the clay suspension. For instance, a highly hydrated lithium cation in the outer swarm, owing to the sheath of water molecules surrounding it, will not be able to approach so near to the inner surface as the slightly hydrated caesium ion. A clay containing lithium ions in the outer cationic swarms of its particles should, therefore, be more stable than a caesium-clay. On this conception it should be expected that the stability of a series of clays would increase in the following order:- hydrogen-clay, caesium-clay, rubidium-clay, potassium-clay, ammonium-clay, sodium-clay, lithium-clay,- if the usual order for the hydration of the various ions is accepted. It also follows that the least hydrated ions would have the greatest coagulating effect, since they can approach more nearly the inner layer, and so can produce a greater reduction of potential. Simple effects of added electrolytes will be obtained only if the added cations are the same as those in the other swarm of the clay particle; in all other cases flocculation effects will be complicated by a base exchange. In order to test these ideas Wiegner carried out an extensive series of experiments with clays /

clays in which the bases had been completely replaced by sodium, ammonium, potassium, and calcium respectively. The sodium-clay was least sensitive to the addition of potassium chloride and the calcium-clay was the most sensitive. In general the clays were found to be more stable, more hydrophilic in character, and less sensitive to electrolytes the greater the hydration of the cations they contained, and the best flocculators were those salts which contained the least hydrated cations. Owing to base exchange small equivalent amounts of potassium and calcium chlorides had the same sedimenting action when added to a large amount of a calcium-clay. These ideas offer a suitable explanation for the different flocculating effects of ions of the same valency and for other divergencies from the Schulze-Hardy Valency Law frequently observed with clay suspensions.

From consideration of figs. 1-6 it will be observed that the correlation between the action of the univalent cations on the rate of sedimentation and the order of the hydration of these ions is not so apparent as in Wiegner's experiments, but, in general, it is in the same direction. The introduction of the highly hydrated sodium ion by means of base exchange into the outer cationic swarm of the kaolin particle produces a more stable suspension than is the case when the slightly hydrated ions of either potassium /

potassium or caesium take the place of some other cations in the outer layer of the particle, and this would account for the fact that sodium chloride is not so effective as either potassium or caesium chlorides in increasing the rate of sedimentation of the kaolin suspensions. A possible explanation of the retardation of the rate of sedimentation at low pH values observed with the ammonium, sodium, and lithium ions may also be found in a similar manner. At low concentrations of sodium chloride the effect of base exchange will not be so great and the sedimenting action of the hydrogen ion will predominate. At higher concentrations of the salt, however, more sodium will be absorbed by the kaolin, and the particles into the outer layer of which the highly hydrated sodium ions are introduced will not be so readily sedimented as the original kaolin particles containing less hydrated cations. As the suspensions were ones which ultimately cleared of themselves, it follows that any differences in the rates of sedimentation were apparent only in the first few hours after the addition of the salts used. In consequence, the retardation observed in the above cases was not so noticeable at the end of half-an-hour, the tubes in which the rate of sedimentation was at first slow ultimately attaining the same degree of clearing as those in which the rate of sedimentation was at first more /

more rapid. Contrary to what would be expected from the relative degrees of hydration of their ions sodium has less effect than lithium in increasing the rate of sedimentation of the suspensions (figs. 1, 2 & 6) and it also has a greater retarding action in presence of acid. It must be remembered, however, that the kaolin was treated with ammonium hydroxide and, consequently, the cations surrounding the particles might be expected to consist largely of ammonium ions. Both the sodium and the lithium ions are more highly hydrated than the ammonium or other ions likely to be associated with the kaolin particles. The lithium ion, being more hydrated than the sodium ion, would not be able to replace the ammonium or other cations as readily as the less hydrated sodium ions, and, therefore, it is possible that in the first few minutes after the treatment with lithium chloride a slightly less stable kaolin would be produced than would be the case after treatment with sodium chloride, the sodium ion being able to enter the outer layer of the particle more rapidly and thus at first to produce a more stable kaolin than the original. This would offer a probable explanation for the slightly greater inhibiting action of sodium in acid medium. It is interesting to note in this connection that in the results of Wiegner's viscosimetric experiments on a calcium-clay given in Table VIII of his paper (loc. cit.) the effect of lithium chloride is in general very nearly equal to that of sodium chloride and within the first six minutes actually exceeds it slightly.

When the sodium ion is coupled with a tervalent anion, as in sodium phosphate or sodium citrate (figs. 11-13), a certain complication is introduced in as far as the pH varies from tube to tube in the row. However, making allowance for this change, two facts emerge:- Firstly, the presence of the tervalent anions obscures the effect of the sodium ion even more than in the case of the bivalent anions, which also have a less pronounced effect in the same direction, e.g. in presence of 0·07 N di-sodium hydrogen phosphate the rate of sedimentation varies from 0 at pH 9·4 to IV at pH 3 to 4. These figures are the same as those obtained when no salt is present. Secondly, the point at which transition takes place from no sedimentation to a marked sedimentation in presence of 0·017 N sodium phosphate and phosphoric acid is about pH 4, and in presence of 0·017 N sodium phosphate and hydrochloric acid it is about pH 5. In fig. 7 with acetic acid alone, this transition point is between pH 5·6 and 8·6. As might be expected the presence of increasing amounts of tervalent anions makes it necessary to reach a higher hydrogen ion concentration in order to effect the same rate of sedimentation. From this point of view the tervalent anions may be looked upon as having a definite protective action. On the other hand, this protective action is barely perceptible if

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we merely consider the effect of the salts at a definite pH. Gengou (1908-9), for example, found that sodium citrate is very potent in retarding the sedimentation of suspensions of barium sulphate. However, in the case of suspensions of kaolin, under the conditions of the experiment, this effect was not nearly so marked. It will be seen from fig. 13 that in acid solution retardation of sedimentation does occur. It will be observed, however, that this effect is almost completely accounted for by the buffering action of the sodium citrate, and that practically no retarding action was evident apart from that due to change of pH. It may be noted that there were present in these acid solutions small amounts of ammonium chloride which may have been sufficient to neutralise any retarding effect. On the alkaline side, so far from there being any protection, readings after half-an-hour showed greater sedimentation in the tubes containing sodium citrate than in those containing none.

Bivalent Cations.

Calcium was chosen as an example of a bivalent cation because of the important use of certain calcium compounds in agriculture. In the simple case of calcium chloride and hydrochloric acid (fig.14) no unexpected features appear. The calcium ion as compared with the sodium ion or the potassium ion is, as one would expect, a much more efficient flocculator. In the case of calcium sulphate and sulphuric acid two figures are given (figs. 15 and 16), the second containing the readings observed for a sedimentation time of 10 minutes, the tubes having been reshaken after standing for a period of 24 hours from the time of the first reading. The differences noted in the alkaline region have been repeatedly verified, and occur also when hydrochloric acid is used instead of sulphuric acid. There is, as would be expected, a certain hindering of the sedimentation by the sulphate ion noticeable in the alkaline region in both figs. 15 and 16, but otherwise the results are substantially the same as those obtained for similar concentrations with calcium chloride and hydrochloric acid. When, however, figs. 17 and 18, dealing with the effect of monocalcium phosphate, are examined, certain peculiarities are at once observed. In the case of monocalcium phosphate and hydrochloric acid the outstanding fact is, that where a concentration of the phosphate /

phosphate greater than 0·005 N is present, the degree of sedimentation is actually increased by increase of pH. At a concentration of 0·02 N there is a change from II at a pH of 2 to V at a pH of 7·9, and at a concentration of 0·08 N a change from a sedimentation of II at pH between 2·4 and 4·2 to one of VI at pH 4·9. If phosphoric acid is used instead of hydrochloric acid, these phenomena are even more marked. It is further to be noted that in the case of these abnormal sedimentations a very bulky and flocculent sediment separated in a very short time, leaving a practically clear supernatant fluid. It seems probable that precipitation of basic calcium phosphate over the surface of the kaolin particles takes place, as a bulky precipitate of the same type separates when a solution of 0·025 N ammonium hydroxide is added to solutions of monocalcium phosphate of the concentrations showing this abnormal effect with kaolin.

In view of the importance of "superphosphate" as a fertiliser, the action of a mixture containing amounts of monocalcium phosphate and calcium sulphate proportionally equivalent to those present in "superphosphate" was investigated (fig. 19). The rather surprising result was obtained that the abnormal sedimentation was even more marked and more extensive as compared with that caused by monocalcium phosphate alone./

alone. In comparing this figure with fig. 17 it is to be observed that whereas the latter commences with a calcium phosphate concentration of 1 per cent (0·08 N), or a calcium ion concentration of 0·16 per cent, the "superphosphate" commences with a total salt concentration of 0·186 per cent. or a calcium ion concentration of approximately 0·04 per cent. At the latter concentration (0·02 N) the monocalcium phosphate alone does not show the effect in nearly so marked a degree. This may be related to the fact that a precipitate of basic phosphate is more easily obtained from the mixture of calcium sulphate and phosphate than from the phosphate alone.

Tervalent Cations.

The results of the experiments with aluminium, ferric, and lanthanum chlorides, represented in figs. 20-22, are similar to those already described in as far as the action in all cases is very different in acid and in alkaline solution. In acid solution the action of the tervalent ion is not marked. This is rather surprising, as these tervalent ions have, as is well known, a powerful flocculating action, but a possible explanation may be that the hydrogen ion alone has a sedimenting action on kaolin so marked that the addition of further ions, however active, is without appreciable effect. In alkaline solutions, on the other hand, the sedimenting effect is practically zero, except at a pH of 7-8, where, if the concentration is appropriate, very marked precipitation occurs. The sediment formed at this point is very bulky, and, as it separates, leaves a very clear supernatant fluid. From the fact that in the case of ferric chloride the precipitate is yellow in colour, and the supernatent fluid has lost its original yellow colour, it is to be inferred that these precipitates contain the metallic hydroxides probably in an absorbed condition. Mere precipitation of the metallic hydroxide by the alkali is not sufficient to effect flocculation of the kaolin, as shown by the fact /

fact that in the cases of iron and aluminium chlorides a precipitate of the metallic hydroxide could be observed in certain tubes although the kaolin was not sedimented at all. At a pH less than 7 a very rapid reduction in precipitation takes place, and, in fact, the particles become protected, and acquire a positive charge at pH between 5 and 3. This is particularly marked in the cases of aluminium and ferric chlorides. In the case of lanthanum chloride the results are slightly different. The regions of precipitation and of protection are not nearly so well defined. In addition, the zone of maximum precipitation was observed after a few days to have shifted towards the region of higher concentration of lanthanum. These differences in the case of lanthanum may be related to the fact that lanthanum hydroxide does not, like aluminium and ferric hydroxides, form stable colloidal solutions at pH between 3 and 7.

These characteristic zones of precipitation which are observed with salts containing tervalent cations resemble very much the zones of precipitation which occur when these salts in the proper concentration and at the necessary pH are added to ordinary colloidal sols such as gold and gum benzion (Kermack and Voge, 1925), a similarity particularly emphasised by the fact that the zone of precipitation separates

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a region where the particles are negatively charged from a region within which they are positively charged. These results are similar to those obtained by Gedroiz (1915) and Comber (1921) with soil clay, and support their views that this characteristic flocculating action of tervalent ions falls into line with the results obtained with ordinary colloids.

The Charge on the Particles and the Iso-electric Point.

It is well known that an electric charge nearly always exists at the boundary surface between a solid and a liquid. This fact was first observed by Reuss at Moscow in 1808 and the phenomenon has been the subject of many investigations since that time. Reuss was using clay diaphragms in water and he noticed that an electric current forced the water through the clay towards the negetaive pole, while any suspended particles of clay migrated towards the positive pole. The first phenomemon is now known as "electrical endosmose" and the second as "cataphoresis". Helmholtz (1879) in the course of a quantitative and mathematical development of the subject put forward the view that under most circumstances a solid in contact with a liquid would become electrically charged, the layer of liquid next the solid having the opposite charge from that of the surface of the solid, thus giving rise to a so-called electrical double layer. Following the work of Reuss and others on electrical endosmose, the study of the motion of the particles of ordinary suspension under an electric field was taken up by various workers and the results of their work is summarised by Wiedemann (1893). It was first clearly demonstrated by Picton and Linder (1892) that the particles of a colloidal solution are /

are electrically charged and it is now generally recognised that such charges play an important part in the properties of colloidal solutions and ordinary suspensions.

The particles of a kaolin suspension in water or in a dilute solution of ammonium hydroxide are negatively charged, and the suspension depends in part at any rate for its stability on the existence of the electrical potential differences between the particles and the dispersion medium. When a suitable quantity of an electrolyte is added to such a suspension these potential differences will be reduced and, the suspension being thus rendered less stable, the rate of sedimentation of the particles will be increased. Complete discharge of the particles does not appear to be necessary in order to obtain entire clearing of the suspension in the shortest time. Kaolin precipitated from suspension by means of tenth-normal calcium chloride was found to be still negatively charged with respect to the solution in contact with it. The results of the work of Ellis (1911 and 1912) and Powis (1914) indicate that when the interfacial potential difference in oil-emulsions is reduced below a certain minimum, flocculation of the oil particles takes place. Similar results were obtained by Powis (1916) with colloidal arsenious sulphide.

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It seems, therefore, that under definite conditions there exists what may be called a "critical potential" below which a suspension or emulsion tends to lose its stability.

The question now arises whether a kaolin suspension possesses an iso-electric point or not. O. Arrhenius (1922) put forward the view that clay could act as an ampholyte and display behaviour analagous to that of proteins according to the explanation of Loeb (1922). He showed that when the rate of settling of clays of different origin and different reaction was plotted against the hydrogen ion concentration the curve had the same course as that for the swelling of gelatine at different hydrogen ion concentrations. He therefore concluded that these clays had the same iso-electric point at which the maximum rate of settling would occur and on either side of which the clays would exhibit basic and acidic properties respectively. Arrhenius apparently did not measure the charge on the particles, and the flocculation experiments on which he based his views can be interpreted in another fashion as pointed out by Bradfield (1923,I). A maximum rate of settling was found by Arrhenius to occur at pH 4-5. Above this point the suspensions became more stable until a pH of about 10 was reached when the rate of settling again increased. Bradfield considers that an excess of electrolyte over the minimum requirement for flocculation increases the volume of the floccule and decreases its specific gravity, and consequently retards /

retards the rate of settling very appreciably. He suggests that the initial swelling is probably due to the setting up of a Donnan equilibrium between the floccules formed on coagulation and the excess of the electrolyte in the solution. On the alkaline side Arrhenius's results are in accordance with the well-known fact that slight traces of alkali hinder the flocculation of clay, while higher concentrations of alkali facilitate flocculation. Bradfield's cataphoresis experiments also afford no support for Arrhenius's view. In two other papers Bradfield (1923,II and 1924) clearly demonstrates by means of conductometric and electrometric titrations that various clays actually behave as true acids. Dayhuff and Hoagland (1924) made a careful series of cataphoresis measurements with a soil clay over a range of hydrogen ion concentrations extending from pH 2.1 to pH 12.7 and found that throughout the whole of this range the clay particles carried a negative charge. It seems certain, therefore, that there are no grounds for attributing amphoteric properties to clays under natural conditions.

In the case of the kaolin suspensions examined in the present series of experiments the particles were found to be negatively charged in the presence of univalent and bivalent cations throughout the whole of a range of hydrogen ion concentrations extending from /

from pH 1.4 to pH 10. As already indicated in the discussion on figs. 20-22 reversal of the charge on the particles does occur in the presence of tervalent cations, and, in accordance with the view of Burton (1916) regarding colloidal solutions of gold, silver, and copper, this might be taken as evidence of the existence of an iso-electric point for kaolin suspensions. It must be remembered, however, that in all these cases reversal of the charge on the particles occurred only in the presence of tervalent ions, and there is no indication that within the range of hydrogen ion concentrations studied a kaolin suspension possesses a definite iso-electric point in the sense that a protein has one.

GENERAL CONCLUSIONS.

The rate of sedimentation of kaolin suspensions as affected by salts may be very different according as the medium is alkaline or acid.

Generally speaking, with low concentrations of salts the rate of sedimentation is greater in an acid medium than in an alkaline one, but tends to become independent of the hydrogen ion concentration with increasing concentration of salt.

For kaolin suspensions the cation is the active sedimenting agent, but the anion with which it is combined is not entirely without effect. The sulphate ion, for instance, hinders the action of the sodium and calcium ions in increasing the rate of sedimentation of the suspensions. In certain cases, as with sodium phosphate and citrate, the hindering effect of the anion is attributable to the buffering action of the salts.

The action of an ion in increasing the rate of sedimentation of the suspensions is, in general, the greater the higher the valency of the ion, but ions of the same valency do not all have the same effect. Among the univalent cations, caesium has a slightly greater sedimenting action than potassium, and potassium is more effective than sodium. These differences can be correlated with the degree of hydration of the ions.

Ammonium /

Ammonium chloride, sodium chloride, and lithium chloride, while increasing the rate of sedimentation in alkaline solution, actually inhibit it in acid solution at concentrations of the salts exceeding 0·06 N. This may possibly be accounted for by the occurrence of an exchange of bases between the added salt and the kaolin and by the difference in the degrees of hydration of the ions.

In certain concentrations of monocalcium phosphate abnormal sedimentation in alkaline or slightly acid solution takes place, with the result that it is much more complete than at the corresponding concentrations in solutions of higher hydrogen ion concentration.

In acid solution the tervalent ions, aluminium, ferric, and lanthanum have little effect, but a zone of very marked flocculation occurs at pH 7-8. This zone separates a region within which the unsedimented particles are negatively charged from a region within which they are positively charged. In all other cases the particles remain negatively charged throughout a range of hydrogen ion concentration from pH 1·4 to 10. Within this range, therefore, a kaolin suspension does not possess an iso-electric point in the sense that a protein has one.

It may be concluded that in studies of the rate of /

of sedimentation of suspensions due attention must be paid to the final hydrogen ion concentration and also to the original reaction of the medium under investigation.

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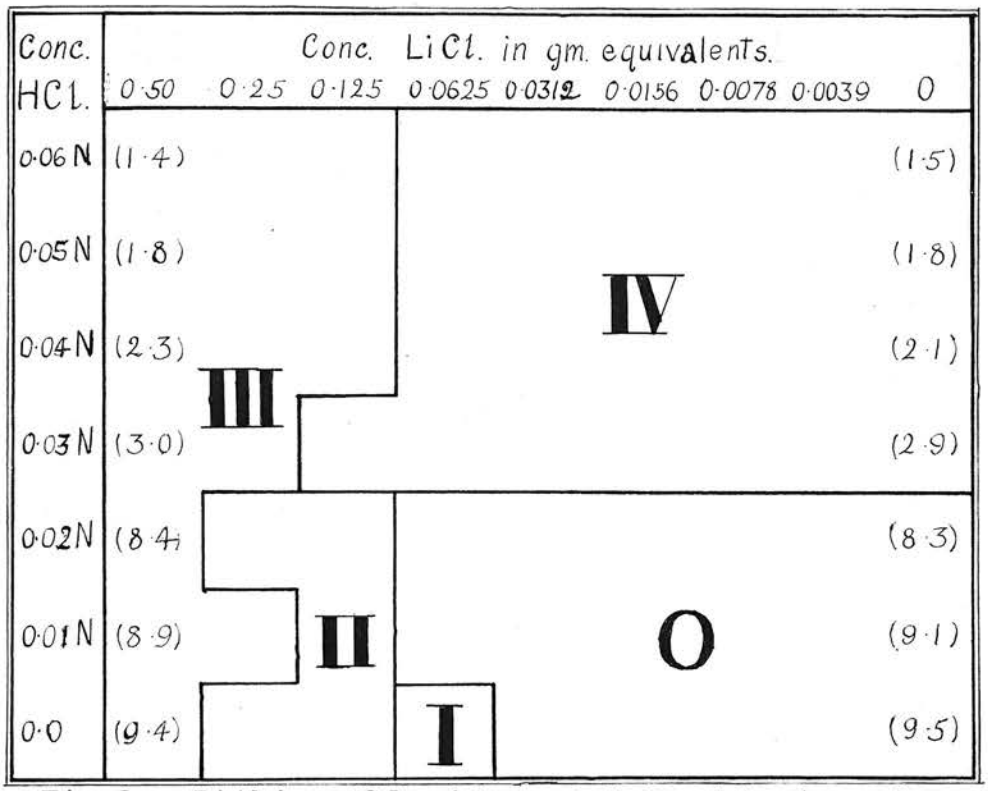

Fig.1.- Lithium Chloride and Hydrochloric Acid.
(Sedimentation after 15 minutes.)

Kaolin per 100 c.c. suspension = 0·44 gm.

(The Roman numerals indicate the degree of precipitation and the ordinary numerals within brackets the pH values)

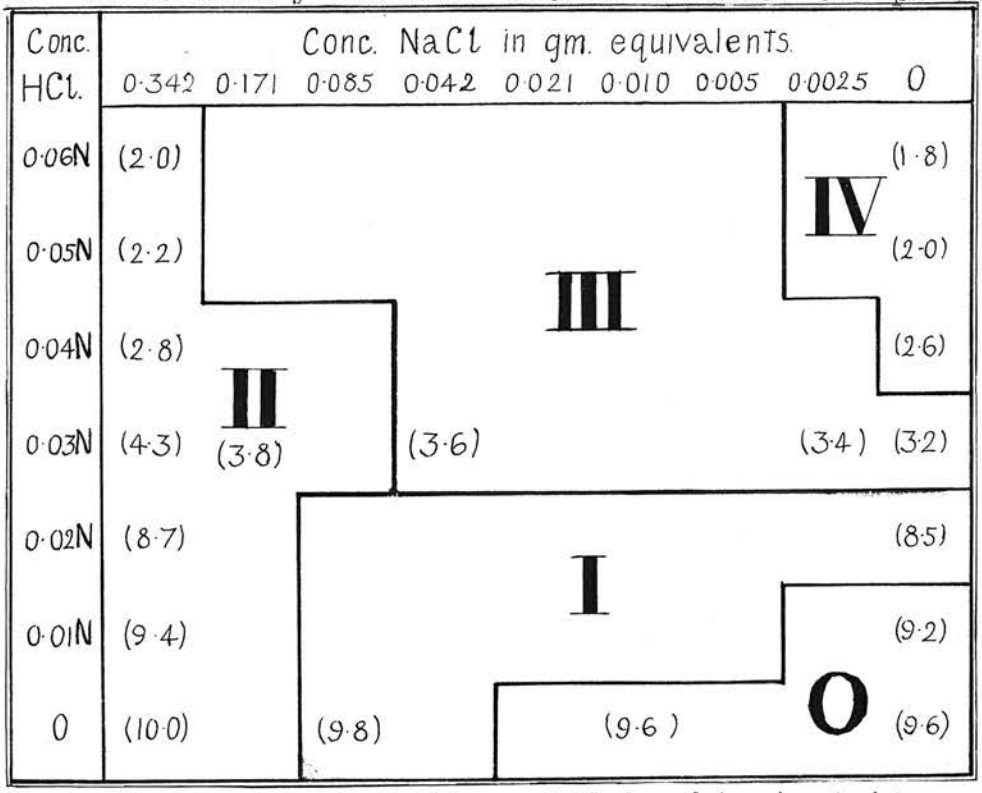

Fig.2.- Sodium Chloride and Hydrochloric Acid.
(Sedimentation after 15 minutes.)

Kaolin per 100 c.c. suspension = 0·35 gm.

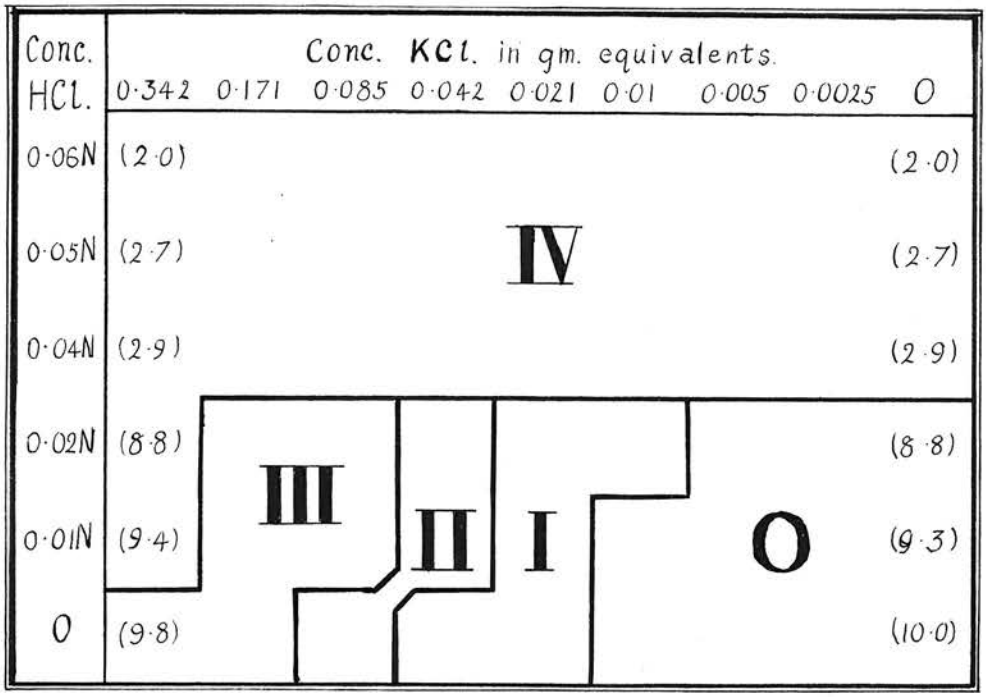

Fig.3.- Potassium Chloride and Hydrochloric Acid.
(Sedimentation after 15 minutes)

Kaolin per 100 c.c. suspension = 0.37 gm.

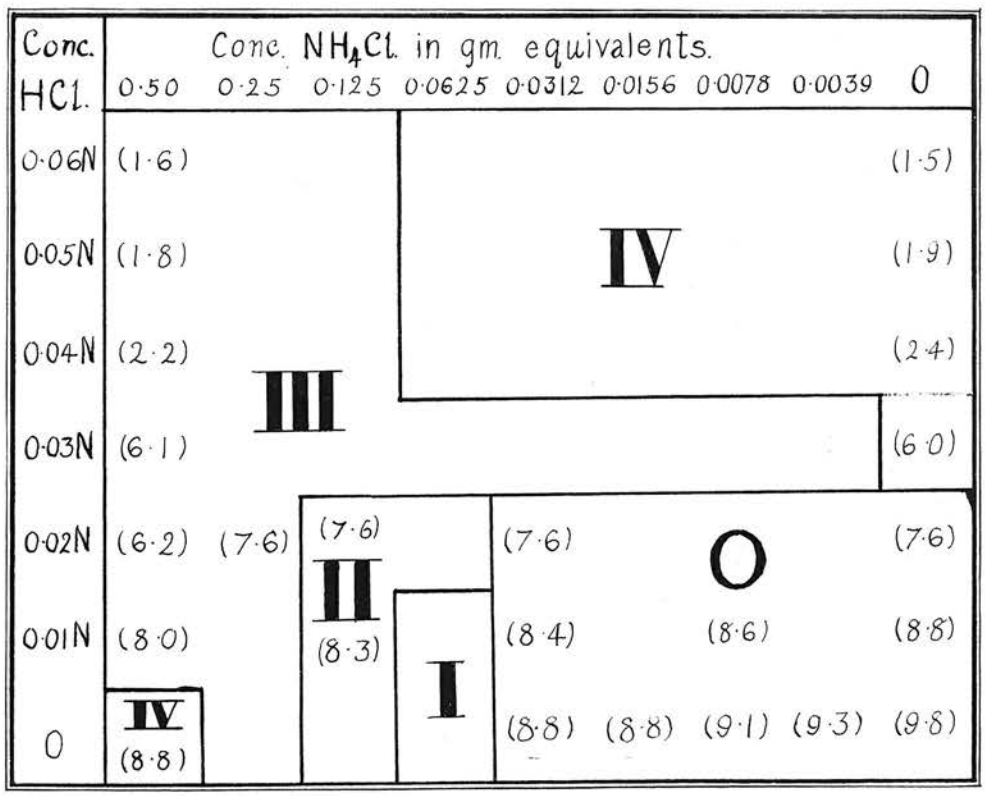

Fig.4.- Ammonium Chloride and Hydrochloric Acid.
(Sedimentation after 15 minutes.)

Kaolin per 100 c.c. suspension = 0·44 gm.

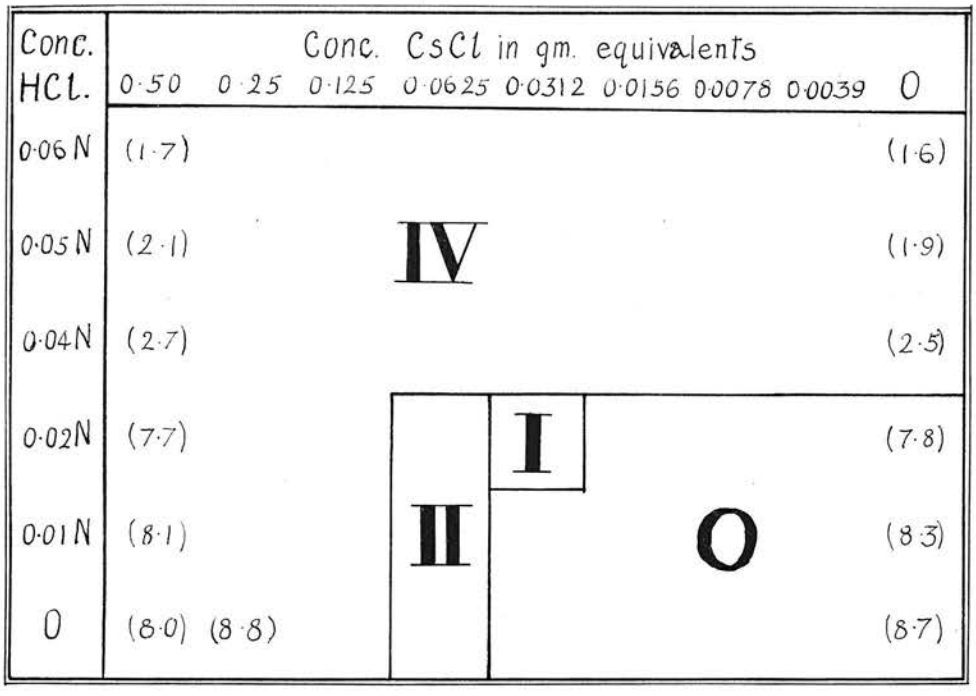

Fig.5.- Caesium Chloride and Hydrochloric Acid
(Sedimentation after 15 minutes)

Kaolin per 100 c.c. suspension = 0·44 gm.

Conc. HCl.	Conc. in gm. equivalents = 0·5.						
	HCl.	CsCl.	KCl.	NH_4Cl.	NaCl.	LiCl.	O
0·06 N	4 (<1·2)	4 (1·9)	3½ (1·9)	3 (1·8)	2½ (2·0)	3 (1·9)	4 (1·9)
0	4 (<1·2)	4½ (8·6)	4 (8·6)	4 (7·9)	3 (8·7)	3 (8·5)	0 (8·4)

Fig.6.- Chlorides of Univalent Metals and Hydrochloric Acid.
(Sedimentation after 15 minutes)

Kaolin per 100 c.c. suspension = 0.44 gm.

(In this figure the numerals in red indicate the degree of precipitation and the numerals within brackets the pH values.)

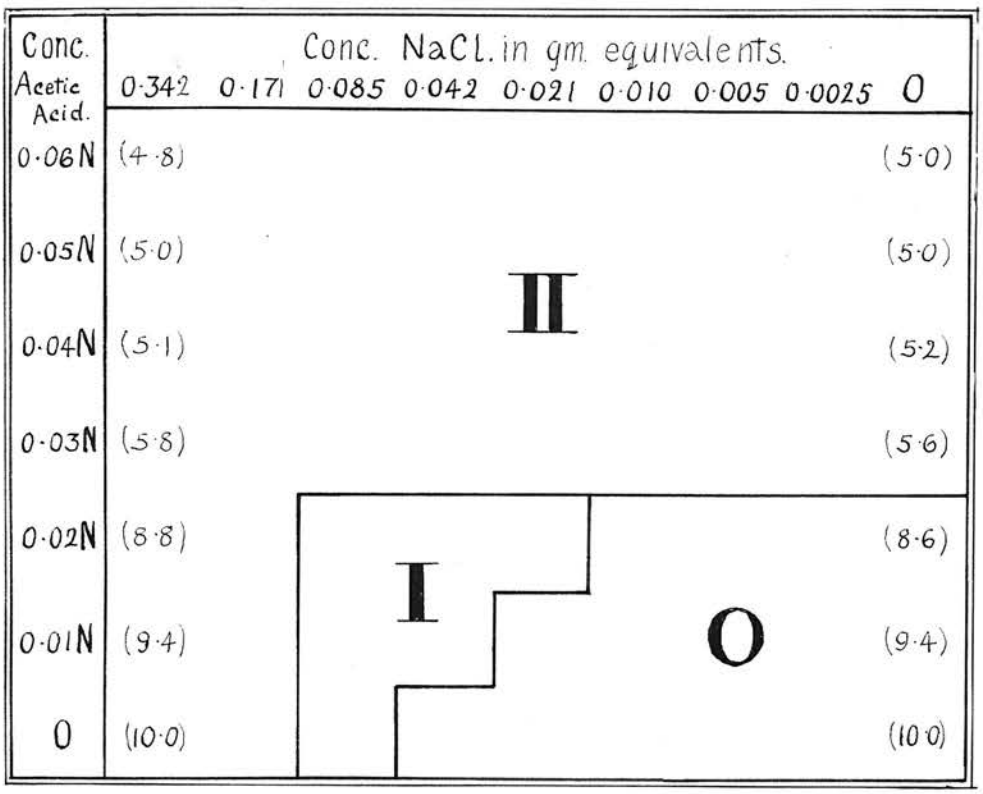

Fig.7.- Sodium Chloride and Acetic Acid.
(Sedimentation after 15 minutes)

Kaolin per 100 c.c. suspension = 0·35 gm.

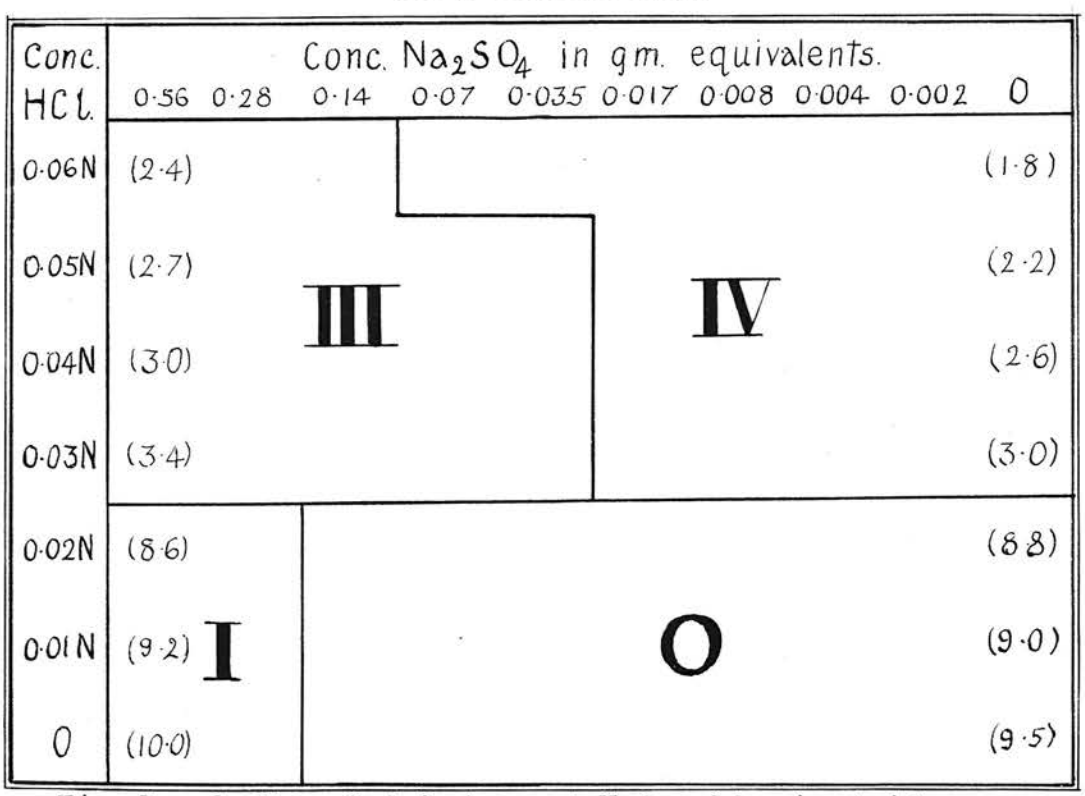

Fig.8.- Sodium Sulphate and Hydrochloric Acid.
(Sedimentation after 15 minutes.)

Kaolin per 100 c.c. suspension = 0.35 gm.

Conc. H_2SO_4	Conc. Na_2SO_4 in gm. equivalents.									
	0·56	0·28	0·14	0·07	0·035	0·017	0·008	0·004	0·002	0
0·06N	(2·6)									(2·0)
0·05N	(2·7)					IV				(2·1)
0·04N	(3·0)									(2·6)
0·03N	(3·4)									(3·0)
0·02 N	(8·4)									(8·4)
0·01 N	(9·3)					O				(9·0)
0	(10·0)									(9·5)

Fig.9.- Sodium Sulphate and Sulphuric Acid.
(Sedimentation after 15 minutes.)
Kaolin per 100 c.c. suspension = 0.35 gm.

Conc. H_2SO_4	Conc. $(NH_4)_2SO_4$ in gm. equivalents.							
	0·50	0·25	0·125	0·0625	0·0312	0·0156	0·0078	0·0039	0
0·06N	(2·1)				IV				(1·8)
0·05N	(2·4)								(2·2)
0·04N	(2·5)	III							(2·4)
0·02N	(7·7)	(7·8)	(8·2)	(8·5)	(8·6)	(8·8)	(9·0)	(9·5)	(9·4)
0·01N	(8·1)	(8·2)	(8·6)	(9·0)	(9·4)	O			(9·6)
0	(8·4)	(9·0)	(9·4)	(9·5)	(9·8)				(9·9)

Fig.10.- Ammonium Sulphate and Sulphuric Acid.
(Sedimentation after 15 minutes.)
Kaolin per 100 c.c. suspension = 0.35 gm.

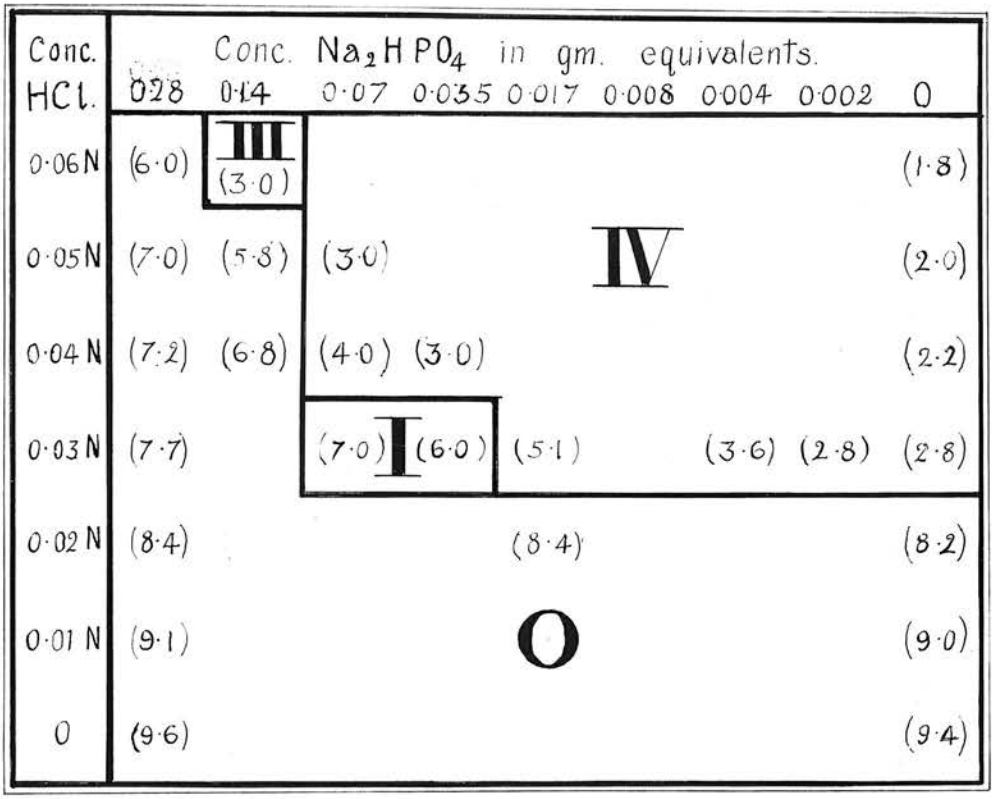

Fig.11.- Di-Sodium Hydrogen Phosphate and Hydrochloric Acid.
(Sedimentation after 15 minutes.)

Kaolin per 100 c.c. suspension = 0.52 gm.

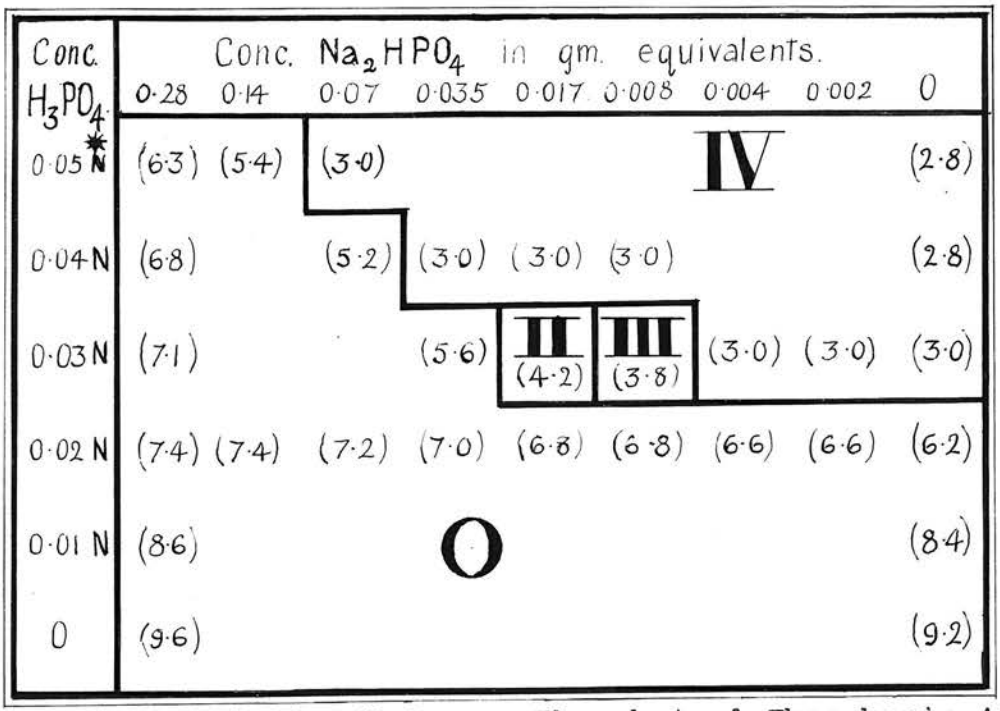

Fig.12.- Di-Sodium Hydrogen Phosphate & Phosphoric Acid.
(Sedimentation after 15 minutes.)

Kaolin per 100 c.c. suspension = 0.52 gm.

*Calculated as monobasic acid.

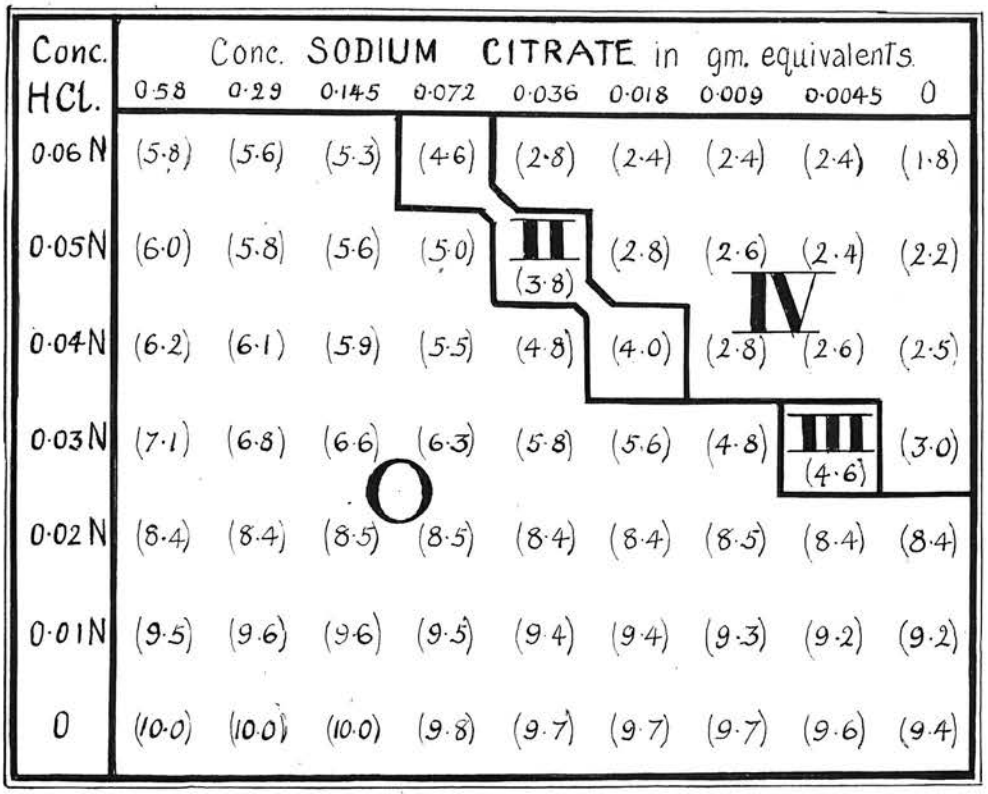

Fig.13.- Sodium Citrate and Hydrochloric Acid.
(Sedimentation after 15 minutes.)
Kaolin per 100 c.c. suspension = 0·37 gm.

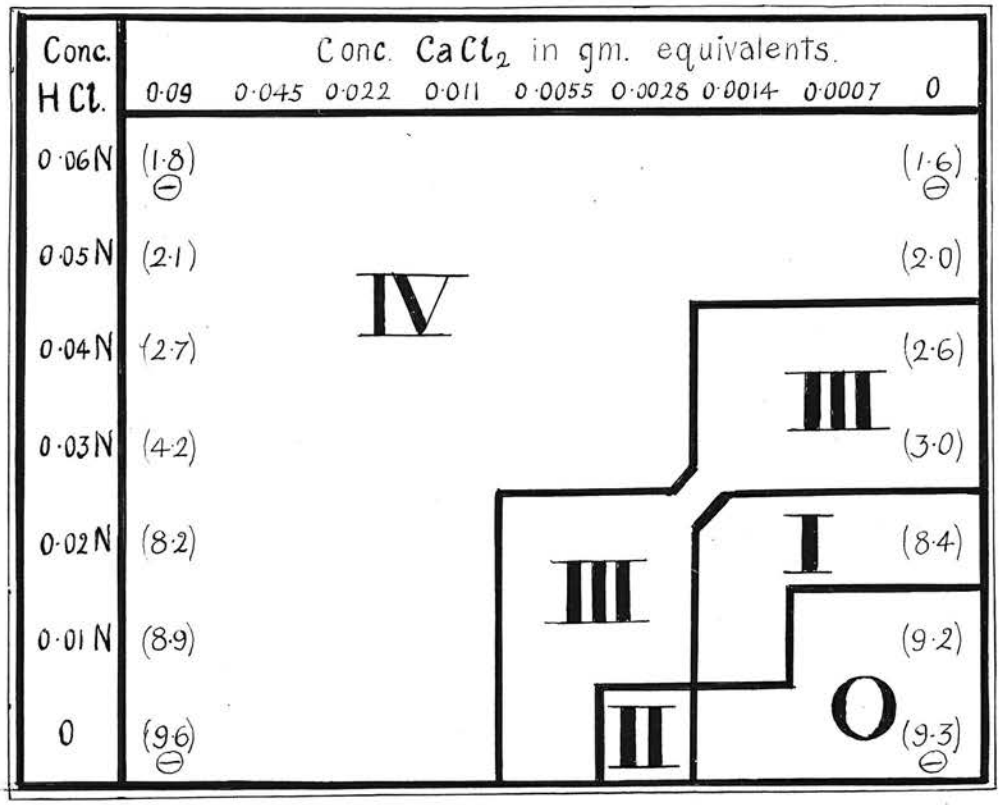

Fig.14.- Calcium Chloride and Hydrochloric Acid.
(Sedimentation after 10 minutes.)
Kaolin per 100 c.c. suspension - 0·35 gm.

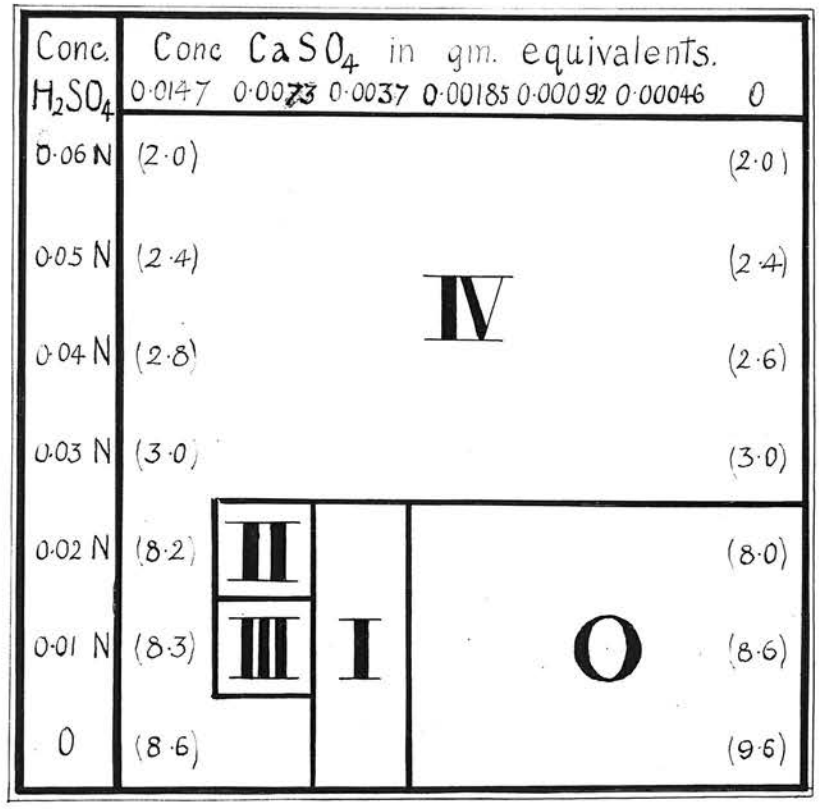

Fig.15.- Calcium Sulphate and Sulphuric Acid.
(Sedimentation after 10 minutes.)

Kaolin per 100 c.c. suspension = 0·52 gm.

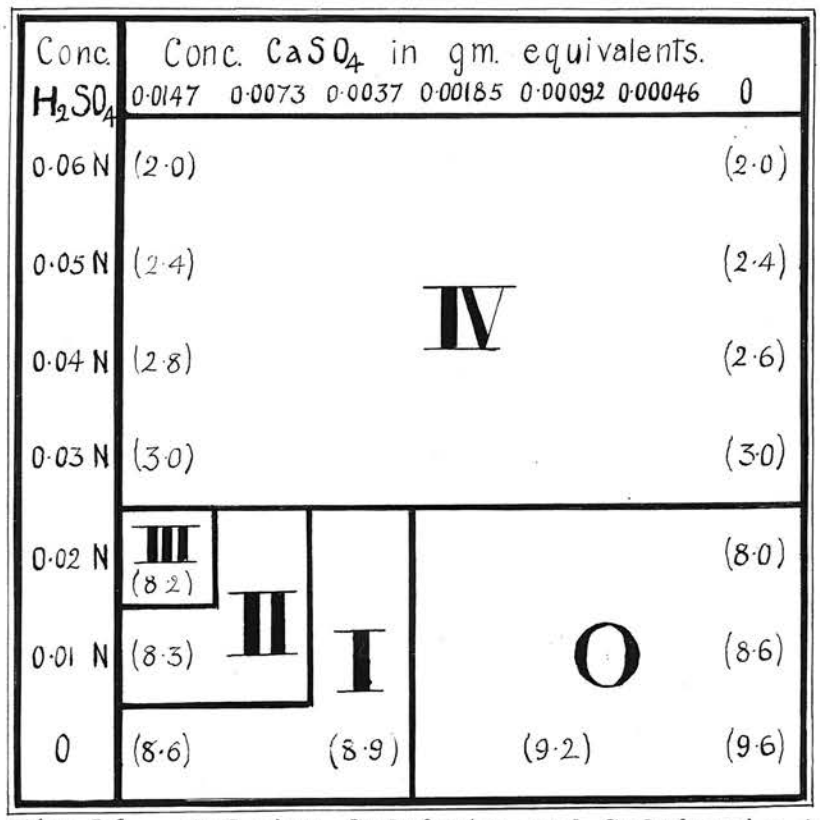

Fig.16.- Calcium Sulphate and Sulphuric Acid.
(Sedimentation after 10 minutes). 24 hrs.later.

Kaolin per 100 c.c. suspension - 0·52 gm.

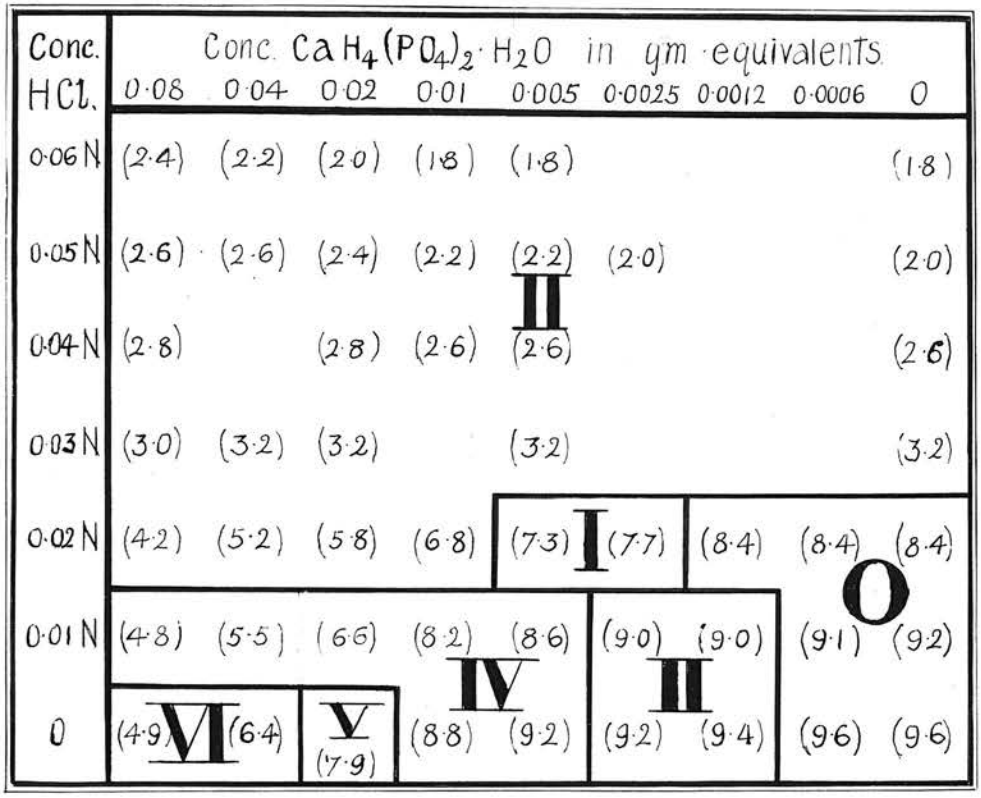

Fig.17.- Monocalcium Phosphate & Hydrochloric Acid.
(Sedimentation after 5 minutes.)

Kaolin per 100 c.c. suspension = 0·52 gm.

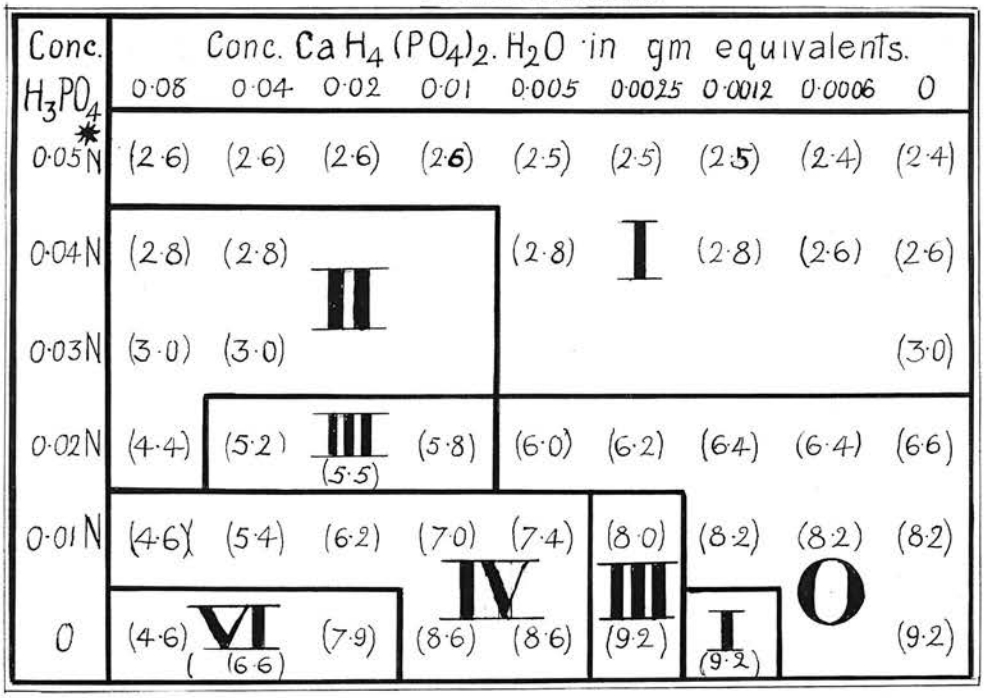

Fig.18.- Monocalcium Phosphate & Phosphoric Acid.
(Sedimentation after 5 minutes.)

Kaolin per 100 c.c. suspension = 0·52 gm.

* Calculated as monobasic acid.

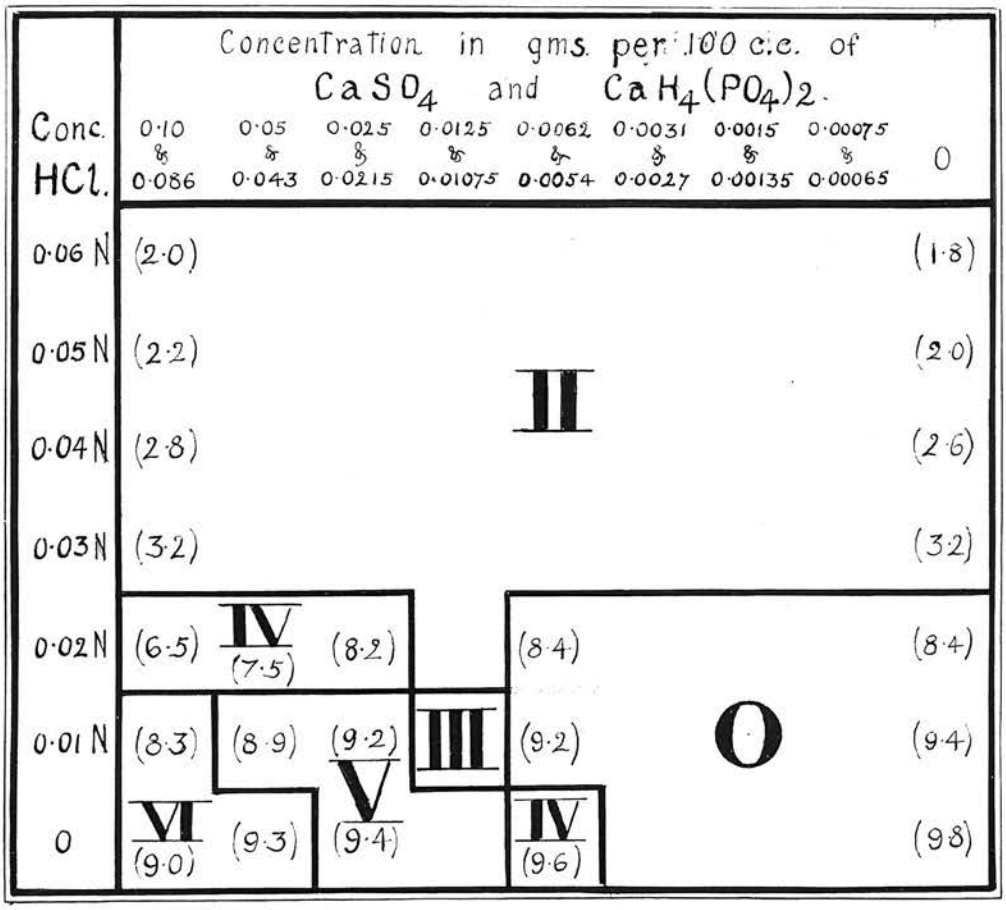

Fig.19.- Calcium Sulphate, Monocalcium Phosphate, and Hydrochloric Acid.
(Sedimentation after 5 minutes.)

Kaolin per 100 c.c. suspension = 0·37 gm.

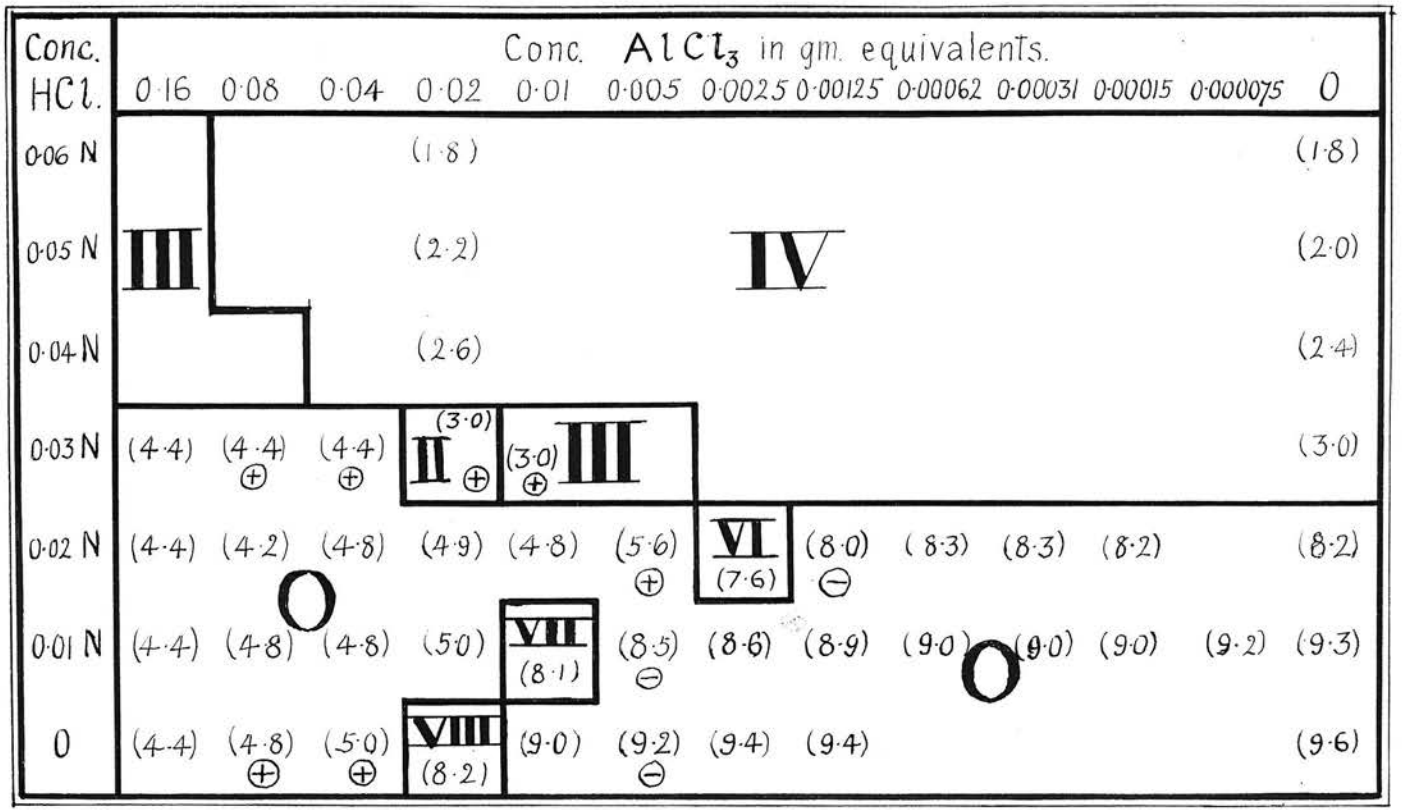

Fig.20.- Aluminium Chloride and Hydrochloric Acid.
(Sedimentation after 10 minutes)

Kaolin per 100 c.c. suspension = 0.37 gm.

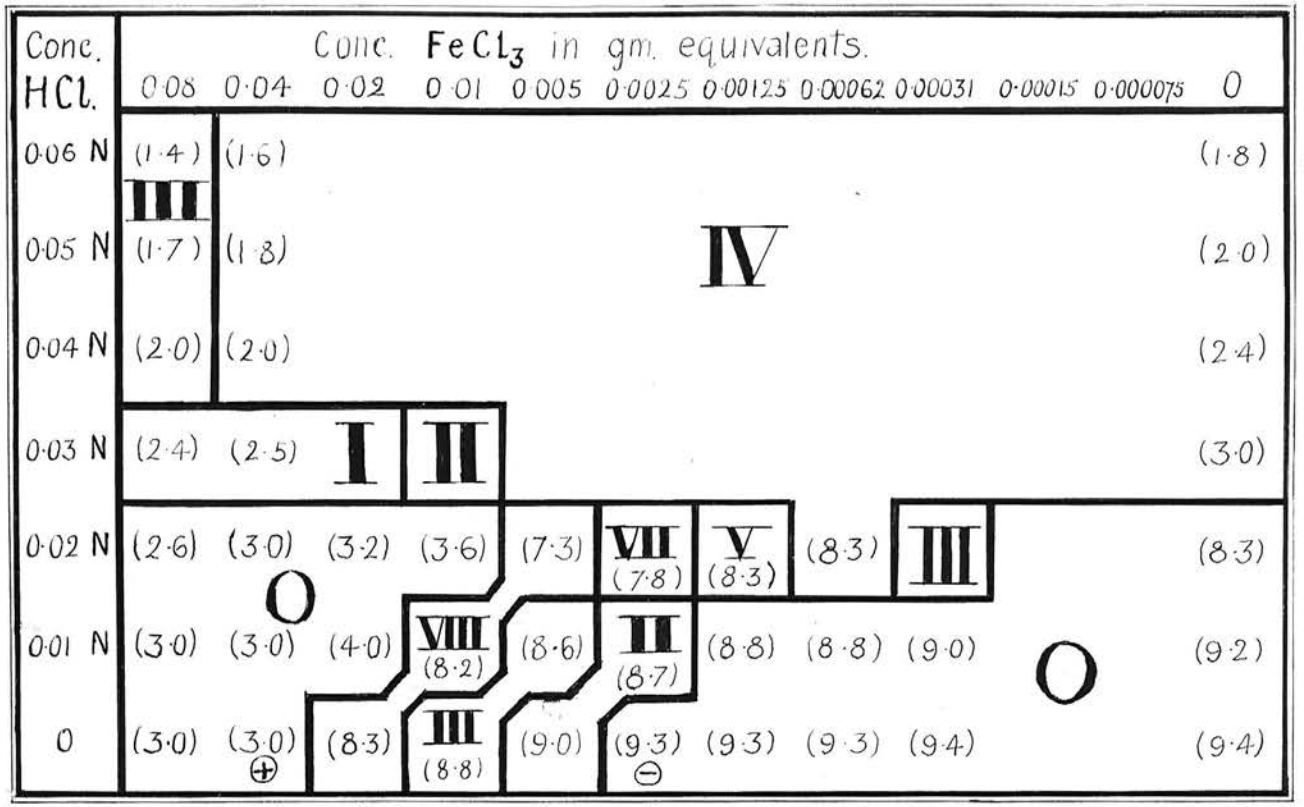

Fig.21.- Ferric Chloride and Hydrochloric Acid.
(Sedimentation after 10 minutes).

Kaolin per 100 c.c. suspension = 0.37 gm.

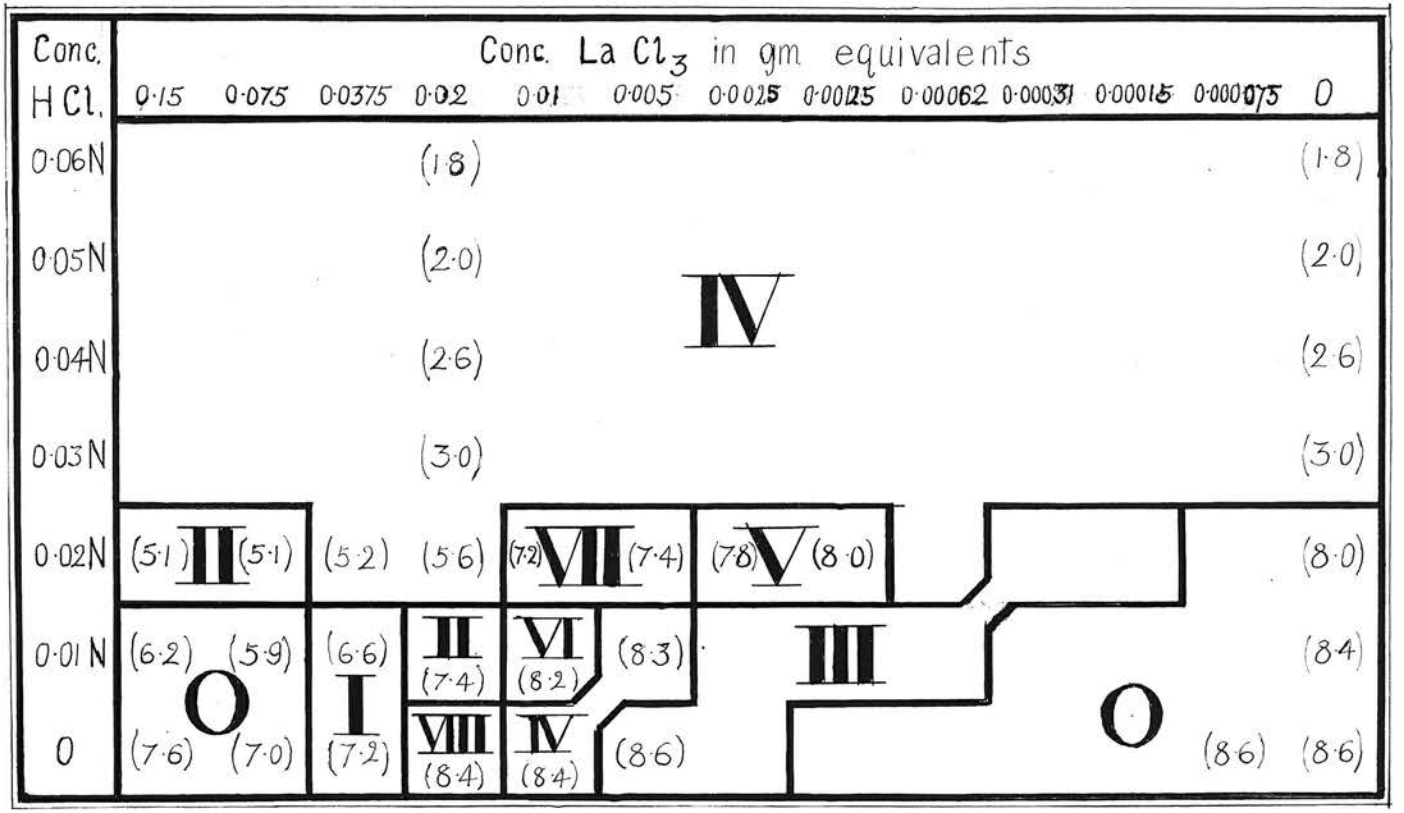

Fig.22.- Lanthanum Chloride and Hydrochloric Acid.
(Sedimentation after 10 minutes).

Kaolin per 100 c.c. suspension = 0.37 gm.